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FULL LENGTH ARTICLE

Water resistance and thermal behavior of metakaolin-phosphate-based geopolymer cements

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ABSTRACT

The main target of this work was to investigate the thermal behavior and water resistance of geopolymer cement made from metakaolin as an aluminosilicate source using phosphoric acid solution (10 M) as a hardener. The obtained geopolymer cements were cured at room temperature for 28 days, the one part was treated at 200°C, 400°C, 600°C, 800°C and 1000°C, and the others were soaked in water for 28 days. The geopolymer cements were characterized by microstructural properties using X-ray diffractometry, infrared spectroscopy, microstructure, physical property based on water resistance and thermo-mechanical properties (thermal analysis, compressive strength). The results show that the compressive strength of the unheated geopolymer cement was 87.96 MPa. The ones soaked in water revealed a strength of 40.71 MPa. This indicates that the specimens soaked in water lose about 54% of their strengths. The X-ray patterns of heated geopolymer cements showed the formation of crystalline phases even at relatively low temperatures. It was typically found that the compressive strength of metakaolin-phosphate-based geopolymer cements decreases due to the hydrolysis of Si-O-P bonds in the presence of water.

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KEYWORDS
Metakaolin; phosphoric acid solution; geopolymer cements; water resistant

1. Introduction

The terrestrial globe is made up of many materials that come from nature including kaolin, volcanic ash, etc. and from industrial by-products including fly ash, slag, etc. which have been used by man in his daily activities such as in construction, energy, medicine, alimentation, etc. The production of ordinary Portland cement (OPC) plays a vital role in our globe. In Portland cement producing industries, the production of a ton of cement liberates approximately a ton of carbon dioxide (CO_2) and other anthropogenic gases such as nitrogen oxide (NO_x) and Sulphur oxide (SO_x) gases which form part of greenhouse gases responsible for global warming [1]. In construction, the demands for modern building materials arise constantly along with lifelong performance properties under different and/or special user conditions, financial aspects such as production and material costs, as well as environmental impact aspects are becoming increasingly important. All these are critical aspects to consider in materials development. For several decades, the search for less expensive, low energy consumption as well as the possibility to reduce the CO_2 emissions during the production of Portland cement has become a major concern leading to the development of new binders so-called geopolymer cements. Some researchers used the raw materials mentioned earlier for producing geopolymer cements for mortars and concretes. These geopolymers can be used in several domains such as civil engineering, automobile industry, metallurgy, waste management, architecture, restoration of buildings, etc. [2,3]. The term geopolymer was introduced by Joseph Davidovits in 1979. However, the similar materials have been synthesized for the first time in 1940 by Purdon. Geopolymer cement is an inorganic polymer consisting of repeating units such as poly(sialate) -Si-O-Al-O-, poly(sialate-siloxo) -Si-O-Al-O-Si-O-, poly(sialate-disiloxo) -Si-O-Al-O-Si-O-Si- created through a geopolymerization process. This inorganic polymer is a material produced by partial dissolution and polycondensation of aluminosilicate precursors in aqueous alkaline solutions [1]. Geopolymers have been proposed as an alternative to OPC for use in construction applications due to their excellent mechanical properties after short periods of hardening [4], low synthesis temperatures and good fire resistance [5,6]. This material is an inorganic polymer binding system that hardens at room temperature similar to paste, mortar and concrete made from OPC [1]. According to Davidovits [7], geopolymer cement can be obtained by two different routes such as in alkaline medium (Na^+, K^+, Li^+,

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Ca^{2+}, Cs^{+}, etc.) and in acidic medium (phosphoric acid solution or humic acids). The synthesized product from phosphoric acid solution as a hardener is called poly(phospho-siloxo) – Si-O-P-O-Si-O-. Studies have shown that the inorganic polymer is obtained after curing the fresh samples for 24 h in an oven at 60°C [8–12]. The thermal and mechanical performance has become an important stake in the use of the geopolymer materials. In recent year, the thermal behavior of geopolymer cements from alkaline solution has been extensively studied [13,14]. The choice of the raw materials, as well as the mechanism, has proven to be a fundamental parameter governing the physicochemical properties consolidating the material. The raw materials widely used are volcanic scoria, metakaolin, fly ash, blast furnace slag, etc. [15]. Recent investigations have shown that the thermal behavior of geopolymers from alkaline solution present good mechanical properties [1], chemical properties [16] and thermal properties [17,18]. The mechanical and microstructural properties of the metakaolin-phosphate-based geopolymer cements have already been conducted yielding suitable properties [8–12]. The water resistance of alkaline-based geopolymers using granite waste as an aluminosilicate source was studied by Tchadjié et al. [19]. They reported that water affected negatively the compressive strength of the granite-based geopolymer cements. Tchakouté et al. [20] also investigated the water resistance of metakaolin-based geopolymer cement using sodium water glass from sugarcane bagasse ash as an alternative hardener. They reported that water does not significantly affect the compressive strength of the metakaolin-based geopolymer cements. Up to now, no previous work has investigated the water resistance and thermal behavior of metakaolin-based geopolymer cements using the phosphoric acid solution as a hardener. Hence, the investigation of thermal behavior and water resistance of geopolymer cements from phosphoric acid solution as a hardener could be interesting. The thermal behavior and water resistance of metakaolin-phosphate-based geopolymer cements were investigated using thermal analysis (differential scanning calorimetric and thermal gravimetric analyzer (TG/DSC)), compressive strength, scanning electron microscope (SEM), water resistance test, X-ray diffractometry and infrared (IR) spectroscopy.

2. Experimental

2.1. Materials

Local clay (Kao) from Littoral region of Cameroon was used as a raw material for producing metakaolin-phosphate-based geopolymer cements. The clay was crushed in a ball mill and sieve to 90 μm followed by calcination in an electric furnace (Nabertherm, Mod. LH 60/14) for 4 h at 700°C (heating/cooling rate of 5° C/min) obtaining metakaolin. The kaolin and metakaolin have already been studied by Elimbi et al. [15] for producing metakaolin-based geopolymer cements. These authors used sodium water glass as a chemical reagent. They reported that this starting material contains kaolinite, quartz, illite, anatase and hematite. The chemical composition of kaolin is given in Table 1.

2.2. Preparation of hardener

Commercial phosphoric acid solution (H_3PO_4 85%, puriss. p.a., Reag. ACS, Reag. ISO, Reag. Ph. Eur. d = 1.60) was used to prepare an acid reactive ingredient or acid hardener. Distilled water was used as a solvent. The reactive ingredient was prepared by dilution of a commercial phosphoric acid solution in distilled water to get a hardener with molar concentration 10 M. The molar concentration of 10 M was chosen according to the conclusion of a previous work [21]. The obtained hardener could mature in the laboratory at room temperature for 4 h prior to use.

2.3. Preparation, casting and curing of geopolymer cement paste

Phosphate-based geopolymer cement pastes were prepared by adding the hardener gradually to metakaolin in a Hobart mixer and mixing mechanically for 5 min. The liquid/solid mass ratio was kept constant at 0.80 obtaining a suitable workability of the paste and the Si:P ratio in the mixture was 0.82. The fresh metakaolin-phosphate-based geopolymer cements were molded into cylindrical PE-containers of dimensions 20 mm in diameter and 40 mm in height. The container was covered with a lid to prevent the evaporation of water during the setting. The container and contents were kept at room temperature for 2 h and then cured at 60°C in an electric oven for 24 h in order to accelerate the polycondensation process. The obtained phosphate-based geopolymer cements were demolding and conserved at room temperature for 28 days before heated and compressive strength testing.

Table 1. Chemical composition of kaolin.

Oxides	Mass composition (wt%)
SiO_2	44.30
Al_2O_3	32.74
Fe_2O_3	7.46
TiO_2	1.90
CaO	0.05
MgO	0.21
K_2O	0.30
Na_2O	1.23
P_2O_5	0.03
SO_3	Trace
Cr_2O_3	0.02
LOI	11.79

LOI: loss on ignition.

2.4. Determination of the thermal behavior of metakaolin-phosphate-based geopolymer cements

The phosphate-based geopolymer cements after curing at 28 days in the laboratory were heated at 5°C/min for 2 h at the following temperatures: 200°C, 400°C, 600°C, 800°C and 1000°C and then allowed to cool within the furnace. The compressive strengths of the calcined geopolymer cements and the ones cured at room temperature were measured. Some portions of the obtained fragments were used for the SEM observations, whereas the other remaining fragments crushed and the resulting powders characterized by X-Ray diffractometer, IR spectroscopy and combined TG/DSC. The geopolymer cements treated at room temperature of 25 ± 2°C and the elevated temperatures i.e. 200°C, 400°C, 600°C, 800°C and 1000°C were denoted GPP2, GPP3, GPP4, GPP5 and GPP6, respectively.

2.5. Water resistance test

To control the water stability of the synthesized products, metakaolin-phosphate-based geopolymer cement after demolded was soaked in water for 28 days before compressive strength testing to evaluate the quality of geopolymer cement using a phosphoric acid solution as a hardener. The pH of water measured at 26, 27 and 28 days were 3, 2.9 and 2.9, respectively, during the test, water was agitated daily. The effect on the compressive strength, microstructure and bonds of phosphate-based geopolymer cement cured at 28 days at room temperature and the one soaked in water for 28 days was also investigated. The sample soaked in water was denoted GPP.

2.6. Methods of characterizations of the starting materials and metakaolin-phosphate-based geopolymer cements

The compressive strengths of unheated and heated metakaolin-phosphate-based geopolymer cements and the ones soaked in water for 28 days were measured using a hydraulic press for cement/mortar machine automatic (Impact Test Equipment Limited) with a 250 kN capacity and loading rate of 0.500 MPa/s. The specimens were subjected to a compressive force until failure. Before compressive strength test, each specimen was polished with sandpaper to obtain a flat and parallel surface. This was done to avoid the nonuniform loading. Eleven samples were tested for each composition and the mean values were determined. After compressive strength measurement, the fragments of each specimen were collected. One part of these fragments was used to observe the morphological changes. The other parts were crushed and the obtained powders were used to measure X-ray diffractometry, thermal analysis (TG/DSC) and IR spectroscopy.

XRD patterns were taken using CuKα radiation between 5° and 80° in 7 h in steps of 0.03° using Bruker D4. IR absorption spectra were taken by the KBr method (200 mg KBr, 1 mg sample, Bruker Vertex 80v, 2 cm^{-1}, 32 scans). TG and DSC of crushed geopolymer cements were performed using alumina crucible between 25°C and 800°C with Seteram Setsys Evolution 1660, technical air with flow 20 ml/min ramping at 10°C/min heating–cooling rate. Pieces from the mechanical testing, after drying and gold coating, were used for microstructure observations using a JEOL JSM-6390A SEM with an acceleration voltage of 30.0 kV.

3. Results and discussion

3.1. Characterization of metakaolin

Figure 1 displays the X-ray pattern of metakaolin (MK-BO_4) and it indicates the peaks of crystalline phases that correspond to illite, quartz, hematite and anatase. It also shows the broad hump structure between 18° and 32° (2θ) centered at around 22° (2θ). The presence of this halo diffraction implies the presence of amorphous phases in the metakaolin.

Figure 2 presents the IR spectrum of metakaolin. It indicates the absorption bands at 458, 595 and 668 cm^{-1}. These absorption bands are ascribed to the bending vibration modes of Si-O-Si. The one at 537 cm^{-1} is attributed to the presence of sialate (Si-O-Al) bonds with Al in sixfold coordination [12,20,21]. The peak at 1076 cm^{-1} is assigned to the asymmetric stretching vibration modes of Si-O-Al and Si-O-Si [22,23]. The absorption band at 817 cm^{-1} is attributed to the bending vibration modes of Si-O-Si. This band can be ascribed to the amorphous silica contained in the structure of metakaolin.

3.2. Characterization of metakaolin-phosphate-based geopolymer cements

3.2.1. Physical aspects of geopolymer cements

The metakaolin-phosphate-based-geopolymer cements cured at room temperature and those heated at 200°C, 400°C, 600°C, 800°C and 1000°C are shown in Figures 3 and 4. It was observed that all specimens exhibited neither deformation nor cracks except the sample heated at 1000°C which showed some cracks, as can be observed on the enlarged image of Figure 4. On the contrary, the investigations of Elimbi et al. [17] reported that the geopolymer cement produced from Cameroonian metakaolin and heated at 1000°C warped, glazed, blistered and exhibited cracks. The specimens heated beyond 200°C indicate the small shrinkage suggesting that the evaporation of the chemically bonded water in these samples. However, from 600°C (Figure 3), the color of

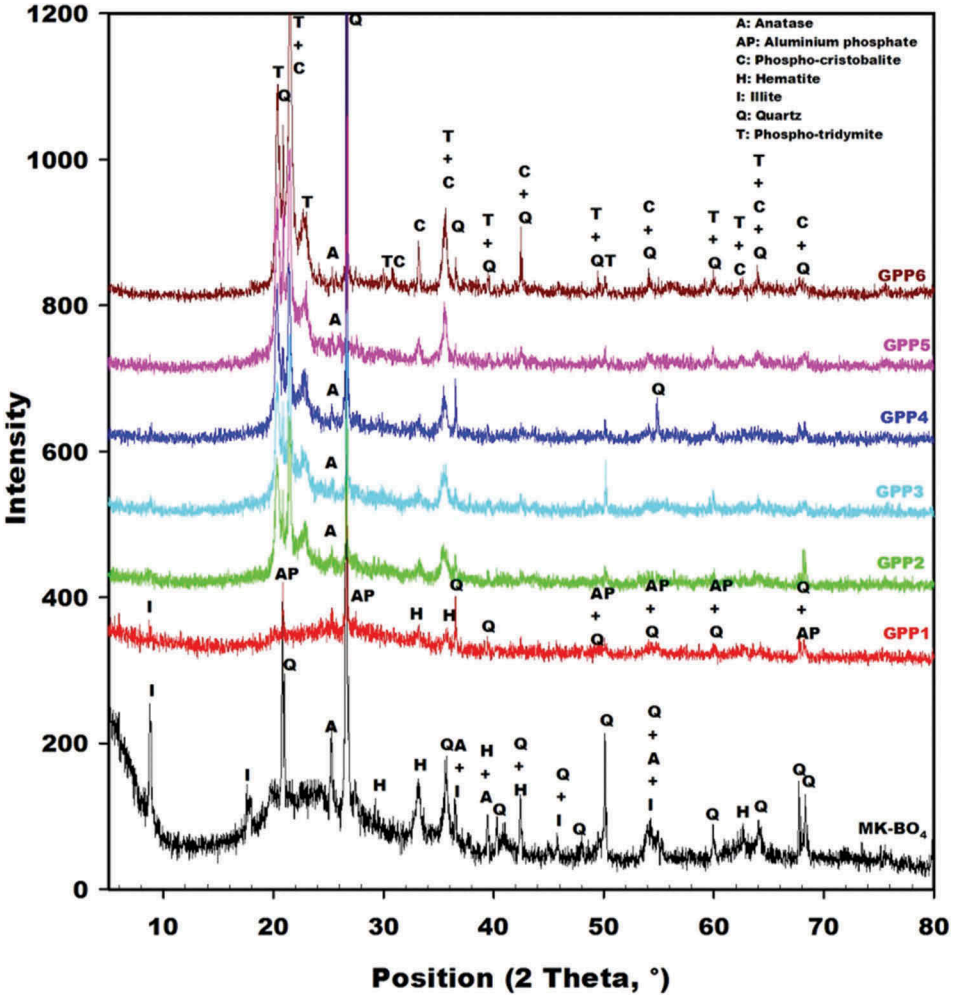


Figure 1. X-ray patterns of metakaolin (MK-BO_4), unheated (GPP1) and heated geopolymer cements (GPP2, GPP3, GPP4, GPP5 and GPP6).

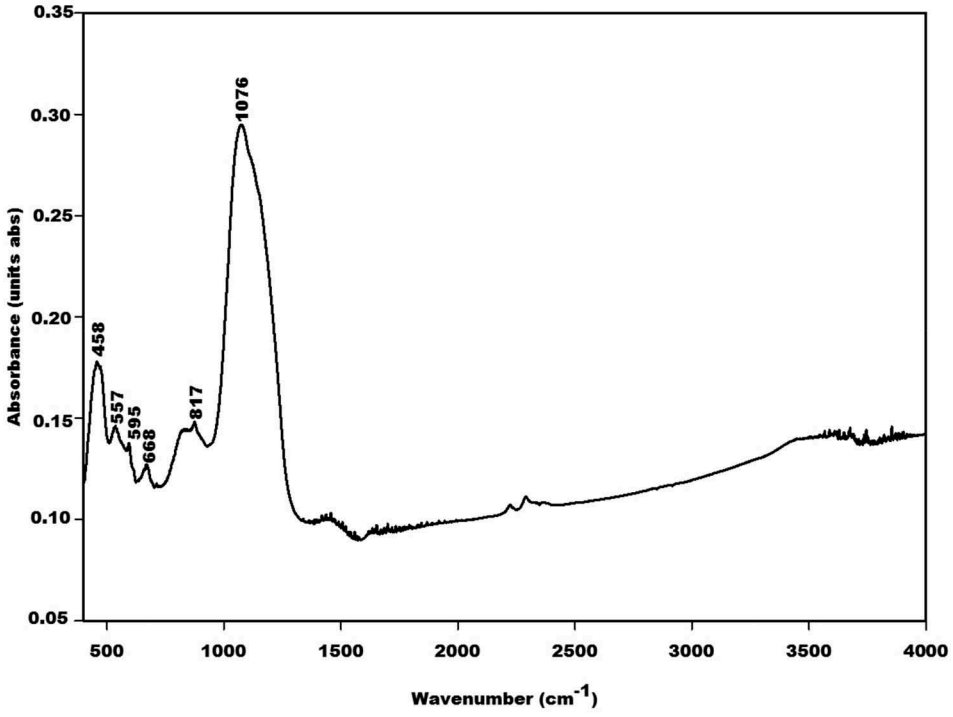


Figure 2. IR spectrum of metakaolin (MK-BO_4).

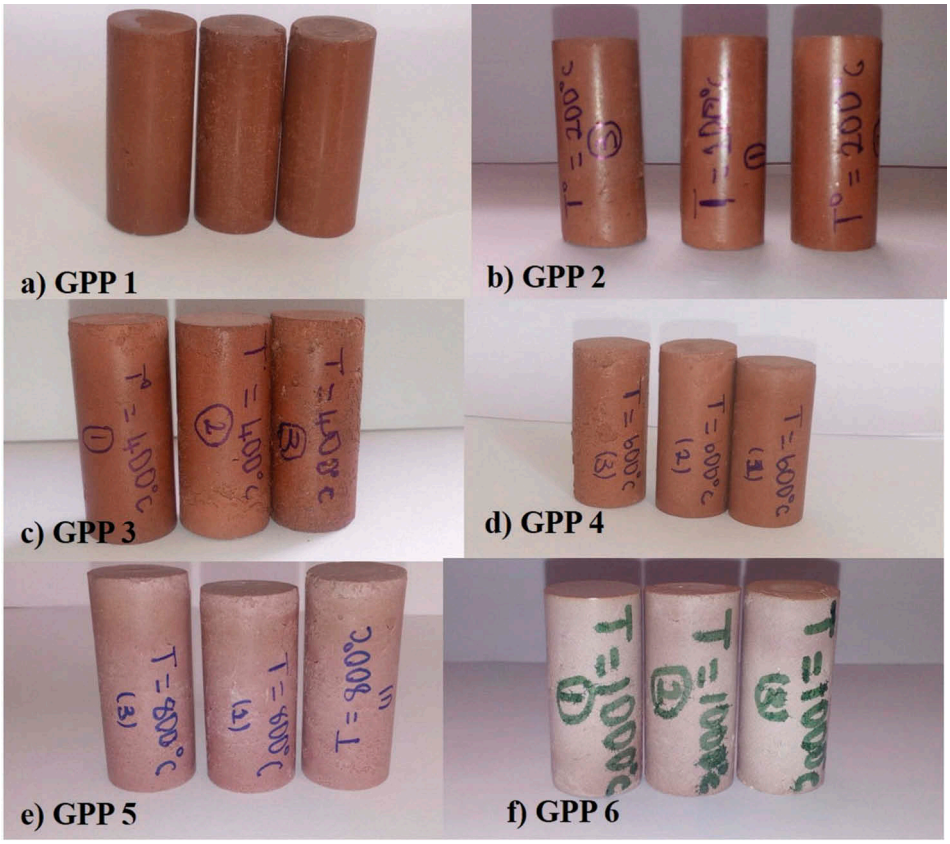


Figure 3. Photos of unheated and heated metakaolin-phosphate-based geopolymer cements. (a) GPP1, (b) GPP2, (c) GPP3, (d) GPP4, (e) GPP5 and (f) GPP6.

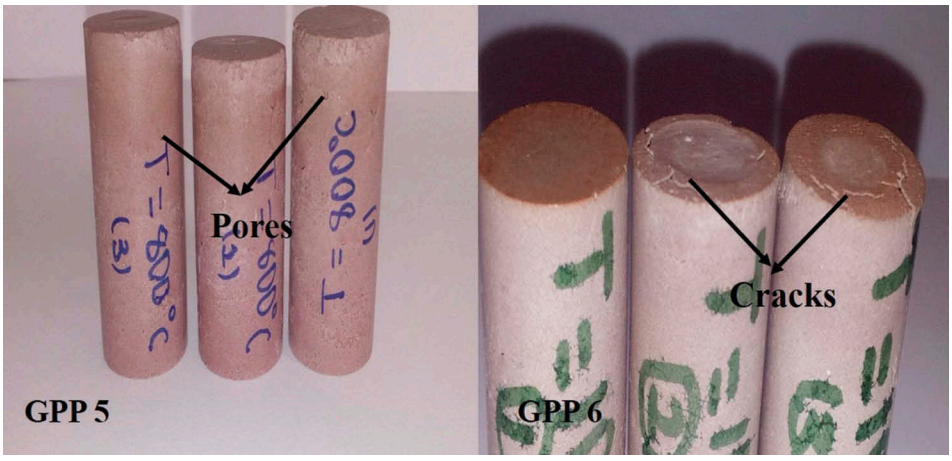


Figure 4. Stretch photos of metakaolin-phosphate-based geopolymer cements heated at 800°C and 1000°C.

geopolymer cement (GPP4) began to lose its coloration tending to the white color. This could be related to the formation of crystalline phase such as phospho-cristobalite ($AlPO_4$) in the structure of the metakaolin-phosphate-based geopolymer cements, as discussed below.

3.2.2. X-ray diffractometry

The X-ray patterns of the metakaolin-phosphate-based geopolymer cements cured at room temperature (GPP1) and those heated at 200°C, 400°C, 600°C, 800°C and 1000°C corresponding to GPP2, GPP3, GPP4, GPP5 and GPP6, respectively, are shown in Figure 1. The X-ray pattern of GPP1 exhibits a typical diffuse halo structure between 20° and 40° (2θ) centered around 26° (2θ). This diffused halo structure appeared between 18° and 32° (2θ) and centered around 22° (2θ) on the X-ray pattern of metakaolin (Figure 1). The slight displacement of this broad hump toward higher degree 2θ on the X-ray pattern of the GPP1 could be related to the modification of the network due to the depolymerization of metakaolin. This modification entails the formation of poly(phospho-siloxo) – Si-O-P-O-Si- 3D network. This implies the depolymerization of metakaolin in the presence of an acidic medium and the reorganization of the structure of

new amorphous materials [8–12,21]. Furthermore, the X-ray pattern of unheated phosphate-based geopolymer cements, GPP1, shows the formation of a new crystalline phase such as berlinite or aluminum phosphate ($AlPO_4$, PDF NO 10-423) [12] which is formed during geopolymerization. It is important to note that berlinite is isostructural with quartz and some peaks of this new crystalline phase are superimposed with the ones of quartz (Figure 1). The X-ray patterns of all metakaolin-phosphate-based geopolymer cements show the peaks of illite, anatase, hematite and quartz which are observed also on the X-ray pattern of metakaolin. This implies that these minerals remain unaffected during the geopolymerization process. The X-ray patterns of geopolymer cements heated between 200°C and 1000°C indicate the disappearance of the aforementioned broad hump structure and the appearance of some crystalline phases such as phospho-tridymite (with the main reflections at 4.36, 4.11 and 3.85 Å, PDF NO 77-0126) and phospho-cristobalite (with main reflections at 4.14, 2.53 and 1.64 Å, PDF NO 02-0278). The formation of berlinite observed on the X-ray pattern of GPP1 is confirmed by the polymorphic transformation of this mineral to phospho-tridymite and phospho-cristobalite on the X-ray patterns of heated metakaolin-phosphate-based geopolymer cements even at relatively low temperature. The formation of phospho-cristobalite confirms the changes in coloration of the samples (Figures 3 and 4) between 600°C and 1000°C.

3.2.3. IR spectroscopy

Figure 5 presents the IR spectra of the unheated and heated metakaolin-phosphate-based geopolymer cements. The IR spectra of the metakaolin-phosphate-based-geopolymer cements display the broad bands at 1638–1628 and 3407–3440 cm^{-1} corresponding to the stretching and deformation vibration modes of H-O-H and -OH, respectively [15,24,25]. The intensity of these absorption bands decreases with increasing the calcination temperature (Figure 5) owing to the evaporation of physically, chemically bonded water and hydroxyl (OH) groups contained in the structure of the specimens. The evaporation of these water could lead to some pores and voids creation in the structure of geopolymer cements, as discussed below. The absorption bands between 475 and 469 cm^{-1} are attributed to Si-O-Si in-plane vibrations. The one at 537 cm^{-1} in the IR spectrum of metakaolin (Figure 1) is ascribed to Si-O-Al^{VI} shifted toward a lower wavenumber after geopolymerization at 523 cm^{-1}. This could be related to the partial replacement of SiO_4 by PO_4 units, resulting in the change in the local chemical environment [10]. This implies the incorporation of the PO_4 unit in the octahedral AlO_6 units during the depolymerization and polycondensation process, indicating the formation of berlinite ($AlPO_4$). This absorption band disappears in the IR spectra of heated geopolymer cements. The disappearance of this band and the appearance of the one at 723 cm^{-1} on the IR spectra of heated metakaolin-phosphate-based geopolymer cements could be assigned to the polymorphic transformation of berlinite to phospho-tridymite and/or phospho-cristobalite. This observation is in agreement with the results obtained on the X-ray patterns of heated geopolymer cements shown in Figure 1. The absorption bands at around 795 cm^{-1} on the IR spectra of all geopolymer cements are assigned to the vibration modes of -Si-O-P- [20]. The presence of this band confirms the formation of the poly(phospho-siloxo) chain in the system. The presence of this band on the IR spectra of all heated geopolymer cements suggests that the calcination process does not destroy the poly(phospho-siloxo) framework. The band at 925 cm^{-1} corresponds to P-OH vibration modes in the structure of geopolymer cements [20]. The intensity of this band decreases on the IR spectra of geopolymer cements heated at 200°C and 400°C but disappears in the IR spectra of the specimens heated at the temperature from 600°C to 1000°C (Figure 5). The reduction of the intensity and the disappearance of this band correspond to the loss of hydroxyl groups in the network of metakaolin-phosphate-based geopolymer cements due to the further polycondensation reaction. The absorption band that appears at 1076 cm^{-1} on the IR spectrum of metakaolin shifted toward higher wavenumber 1085, 1124, 1125, 1122, 1122 and 1121 cm^{-1} (called density of states peak maximum, DOSPM, in the following) for GPP1, GPP2, GPP3, GPP4, GPP5 and GPP6, respectively. The shift of the DOSPM implies the change of the microstructure due to the depolymerization and polycondensation process for GPP1 and the calcination process for the other geopolymers. The increase of the DOSPM from 1085 to 1125 cm^{-1} on the IR spectra of unheated and heated metakaolin-phosphate-based geopolymer cements (Figure 5) could be related to the inclusion of phosphorus (P) and/or silicon (Si) in the network of the specimens leading to the formation of poly(phospho-siloxo) for GPP1 and phospho-tridymite and phospho-cristobalite for the heated geopolymer cements, as can be confirmed on the X-ray patterns of unheated and heated geopolymer cements (Figure 1). The presence of these crystalline phases is also confirmed by the narrow bands of the DOSPM observed on the IR spectra of heated geopolymer cements. The shoulder bands that appear at 1051 cm^{-1} in the IR spectra of GPP5 and GPP6 (Figure 5) and more pronounced on the IR spectrum of GPP6 could be related to the formation of phospho-cristobalite in the network.

The IR spectra of the metakaolin-phosphate-based-geopolymer cement soaked in water (GPP) and the one cured at room temperature (GPP1) are given in Figure 6. Both IR spectra are similar (same wavenumber). But, the intensity of the absorption band at about 1638 and 3407 cm^{-1} increases owing to a significant uptake of water when metakaolin-phosphate-based geopolymer cement was soaked.

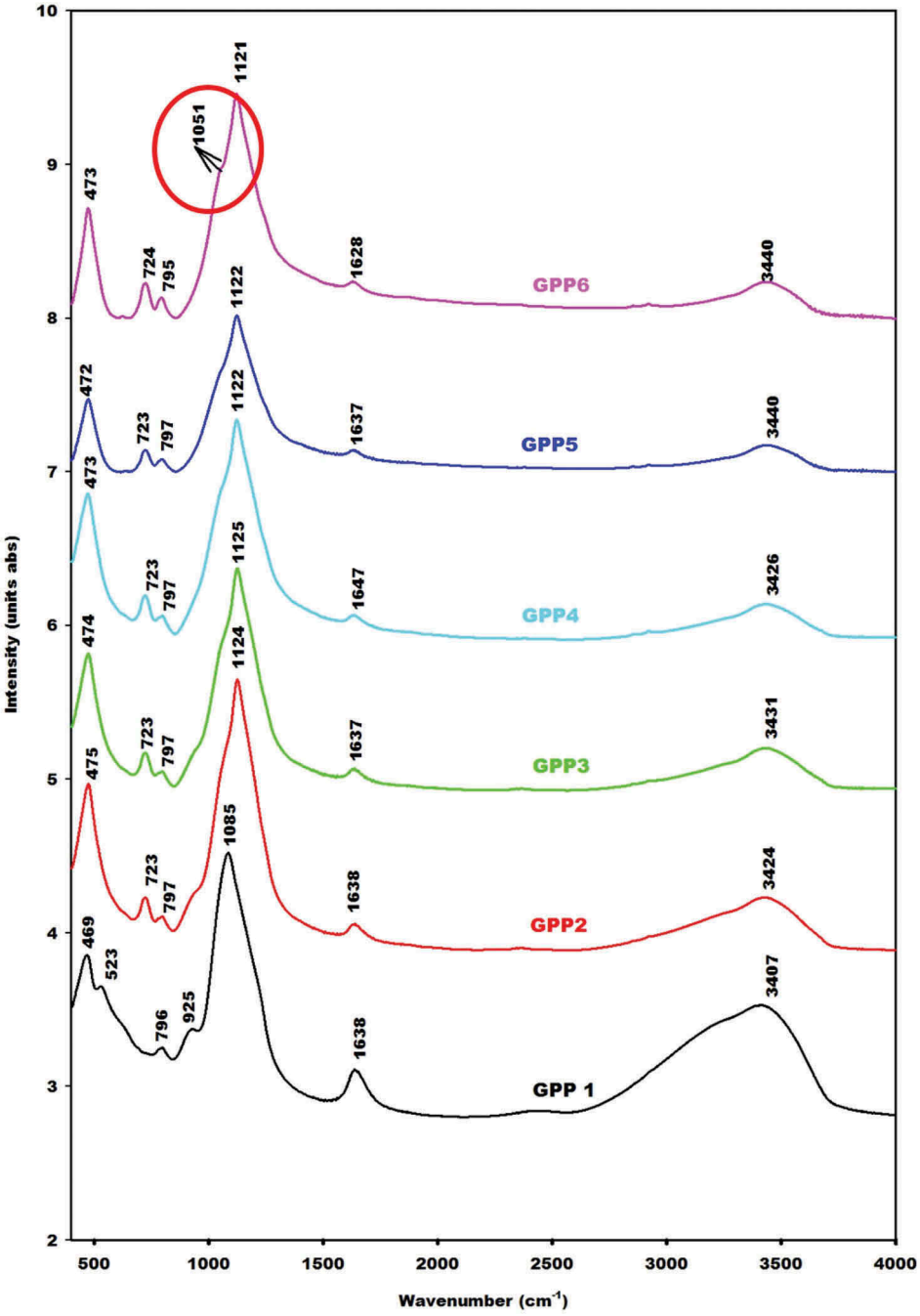
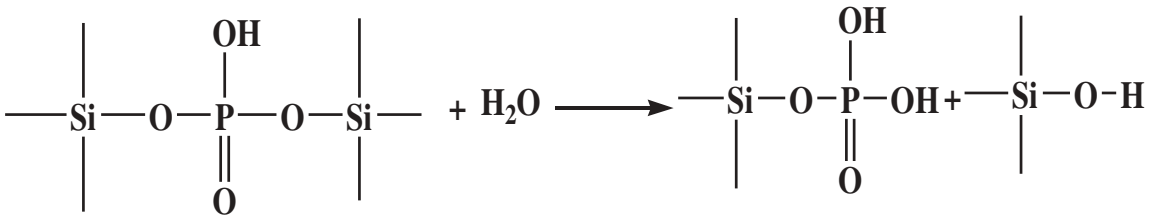


Figure 5. Infrared spectra of metakaolin-phosphate-based geopolymer cements.

This could be attributed to the hydrolysis of Si-O-P bonds leading to the formation of silanol (Si-OH) and P-OH groups in the geopolymer network according to the following equation:

The formation of this silanol and P-OH groups could affect the strength of geopolymer cement soaked in water, as discussed below. It appears that water does not affects significantly the absorption band at about 950 cm^{-1} (P-OH) of metakaolin-phosphate-based geopolymer network.



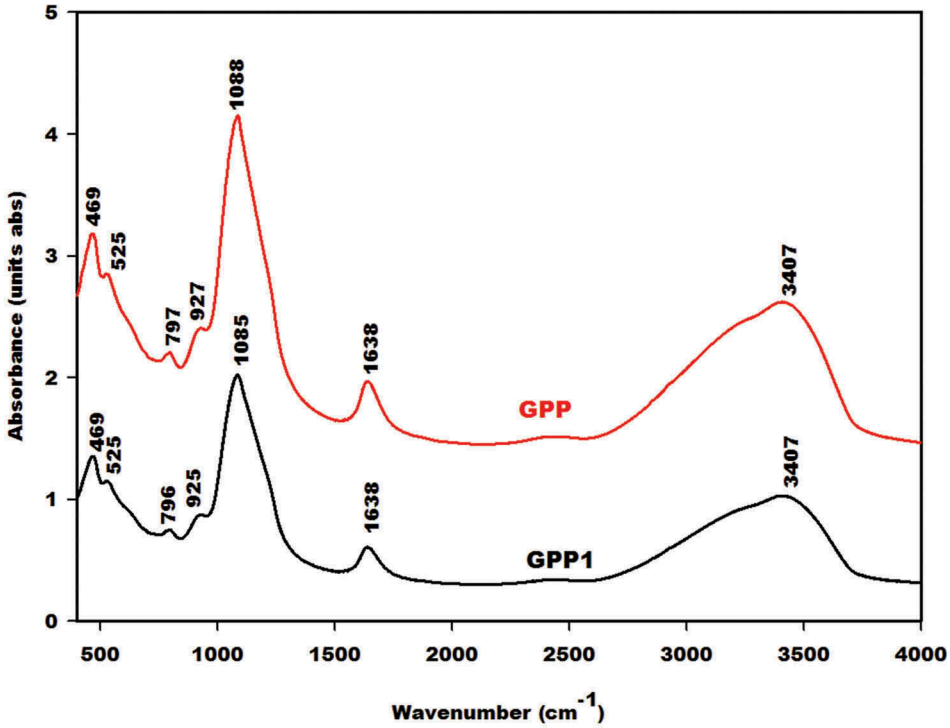


Figure 6. Infrared spectra of geopolymer cement soaked in water (GPP) and the one cured at room temperature (GPP1).

3.2.4. Thermal analysis

TG and DSC curves of unheated and heated metakaolin-phosphate-based geopolymer cements are shown in Figure 7. The major mass loss is observed at the temperature between 100°C and 150°C with a maximum of about 130°C. The TG curves of the unheated and heated geopolymer cements contain three types of water that will escape during the heating process. Physically and chemically bonded water escape at temperatures between 25–100°C and 100–300°C, respectively. Hydroxyl groups also appear at the temperatures beyond 300°C [7,26]. This implies that all specimens contained the aforementioned types of water in their network indicating that metakaolin-phosphate-based geopolymer cements could have a good high-temperature performance. It is important to note that the TG and DSC curves of heated metakaolin-phosphate-based geopolymer cements exhibit the mass loss at about 130°C (Figure 7). This implies that the heated metakaolin-phosphate-based geopolymer cements contain chemically bonded water or structural water in their network even at a relatively high temperature (Figure 7). This is in agreement with the IR spectra results which show always the absorption bands at about 1632 and 3500 cm^{-1} as depicted in Figure 7. The presence, particularly of the chemically bonded water in the poly(phospho-siloxo) network, could affect positively their mechanical properties and stabilize the network [26]. The endothermic phenomenon and the mass loss which appear between 25°C and 200°C (Figure 7) for all geopolymer cements indicates the removal of physically absorbed water, physically bonded water and the one part of the chemically bound water in the poly(phospho-siloxo) network. The weak endothermic peak observed at about 220°C only in the DSC curve of unheated geopolymer cements but not clearly appears on the TG curve corresponds to the mono-aluminum phosphate undergoes transformation to amorphous phase [27–29] and small amounts of hydrated aluminum phosphates can be formed [29,30]. This result confirms the formation of berlinite during the geopolymerization process, as can be seen on the X-ray pattern (Figure 1) and the IR spectrum (Figure 5) of unheated geopolymer cement, GPP1. A weak exothermic phenomenon observed at 400°C, 500°C, 650°C and 950°C in the DSC curve of unheated specimens (Figure 7) is ascribed to the formation of phospho-tridymite and phospho-cristobalite in the structure of poly(phospho-siloxo). This is in agreement with the results of X-ray patterns (Figure 1) and the IR spectra of the heated specimens (Figure 5) which show the peaks of these crystalline phases. A weak endothermic peak which appears at around 590°C on the DSC curve of GPP1 corresponds to the polymorphic transformation of α-berlinite to β-berlinite [31,32]. The mass loss beyond 300°C observed on the TG curves of all geopolymer cements could be assigned to the further condensation of P-OH groups observed in the structure of metakaolin-phosphate-based geopolymer cements. This further condensation reaction has been observed on the IR spectra of metakaolin-phosphate-based

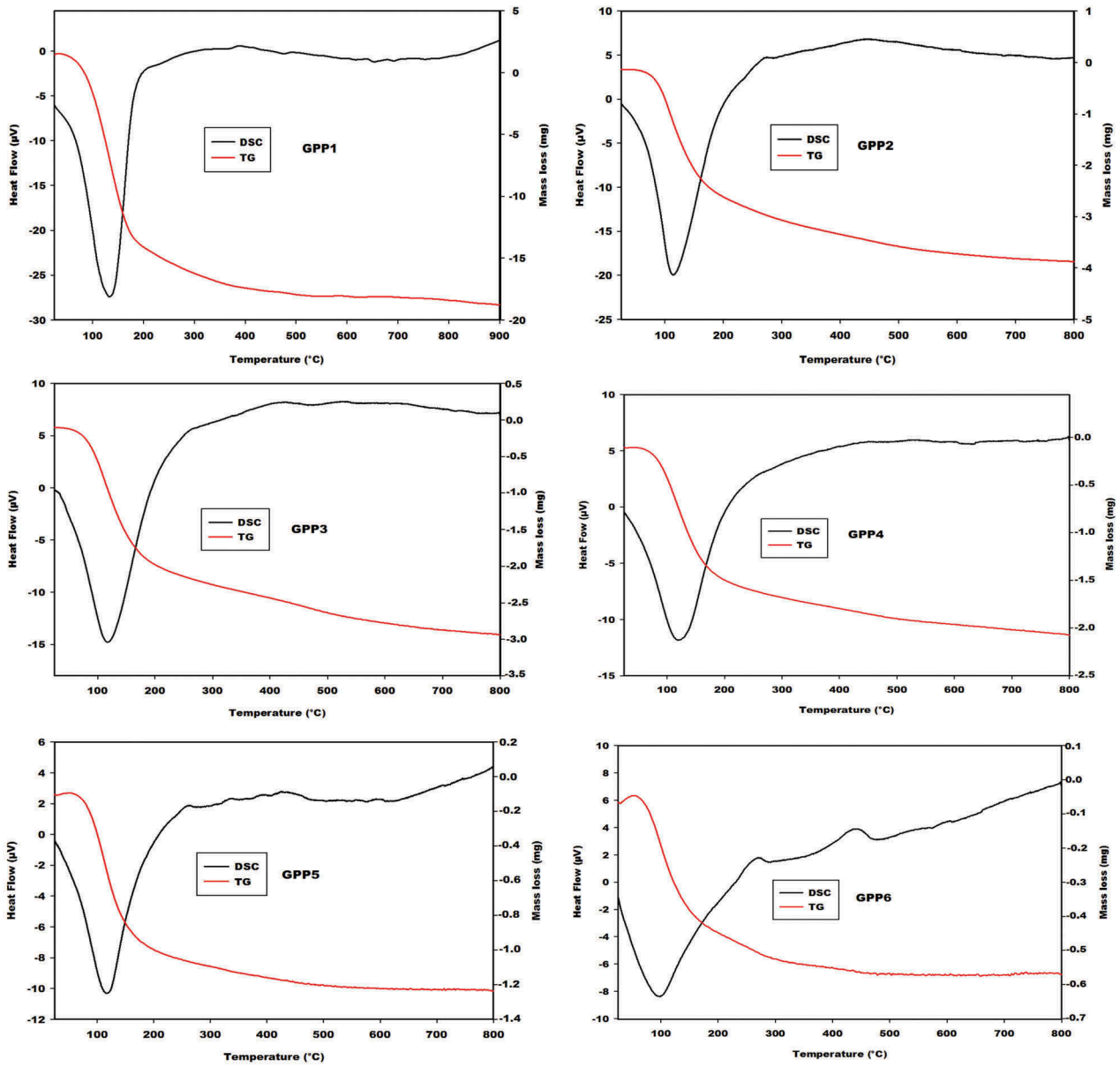


Figure 7. TGA and DSC curves of unheated and heated metakaolin-phosphate-based-geopolymer cements.

geopolymer cements by the reduction of the intensity and/or the disappearance of the band at about 925 cm^{-1} (Figure 5). Similar results have been obtained by Prud'homme et al. [33]. It is important to note that these authors used alkaline solution to prepare geopolymer cements.

3.2.5. Compressive strength

The values of the compressive strengths of the unheated (GPP1), heated (GPP2, GPP3, GPP4, GPP5 and GPP6) and the one soaked in water for 28 days (GPP) of metakaolin-phosphate-based geopolymer cements are shown in Figure 8. The water resistance of geopolymer cement has been defined as one of the key tests for assessing the use of this material [19]. Tchadjié et al. [19] attempted to investigate the water resistance of geopolymer mortars from granite waste as aluminosilicate source. They reported that the compressive strengths of some specimens cured at room temperature during 28 days were about 21.25 and 40 MPa, but after soaking in water, they observed the formation of cracks and meanwhile, the other crumble within 48 h of immersion period. In the present study, the geopolymer cement after soaking in water for 28 days remains a consolidated material but the compressive strength decreases from 87.71 (for the specimens cured at room temperature) to 40.71 MPa (for the specimens soaked in water) (Figure 8). This could be related to the easy hydrolysis of Si-O-P bonds in the presence of water [34]. This corroborates the result obtained on the IR spectrum of GPP (Figure 6) which indicates the higher intensity of the bands at 1638 and 3407 cm^{-1} (following the reaction H_20 + Si-O-P Si-OH + H-O-P). It appears that the compressive strength of metakaolin-phosphate-based geopolymer cements dropped

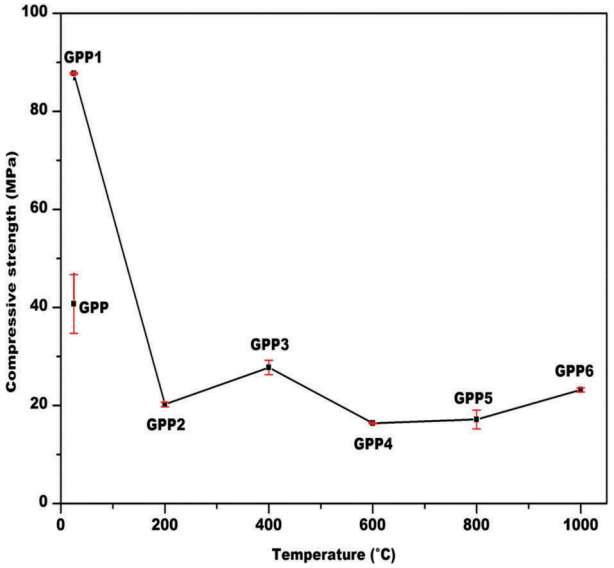


Figure 8. Compressive strength of metakaolin-phosphate-based geopolymer cements.

at approximately 54% after immersion in water for 28 days. This implies that water affects the poly (phospho-siloxo) network. Davidovits [7] reported that geopolymer cements from alkaline solution lose about 30% of their compressive strength after soaking in water from 24 h to 4 days. Despite the compressive strength of metakaolin-phosphate-based geopolymer cement soaked in water lose about 54% on its strength, the value of its strength remains higher (40.71 MPa) like Portland cement 42.5 suggesting thus this specimen could be used for the building materials.

The compressive strengths of geopolymer cements decrease drastically from 87.96 MPa for GPP1 to 20.2 MPa for GPP2 (geopolymer cements heated at 200°C). This indicates that during the heating process, geopolymer cements losses abruptly the higher amount of the physically and chemically bonded water in their structure. The evaporation of these water induces the formation of the pores in the structure of the samples [35,36], which could be responsible for the reduction of the values of the compressive strength (Figure 8). The reduction of strength from ambient temperature to 200°C could also be attributed to the sudden loss of physically and one part of chemically bonded water in the structure of metakaolin-phosphate-based geopolymer cements. Above 200°C, the compressive strength values are not the same since there is no overlapping of error bars when considering the lower and higher values of the standard deviation implying the results are significant. Above 200°C, the strength increases from 20.2 to 27.76 MPa. The increase of the compressive strength from 200°C to 400°C can mainly be attributed to the further polycondensation reaction which densified the structure of geopolymer cements. This is a good agreement with the IR spectrum of the geopolymer cements heated at 400°C, GPP3, which shows the reduction of the intensity of the shoulder absorption band that appears at 925 cm^{-1} (Figure 5). The compressive strength decreases at the temperature above 400°C suggesting the disappearance of the total hydroxyl groups in the network, as can be seen in the IR spectrum of the geopolymer cements heated at 600°C, GPP4 (Figure 5). Beyond 600°C, the strengths increase slightly from 16.39 (for geopolymer cements heated at 600°C) to 17.14 MPa (for geopolymer cements heated at 800°C) and from 17.14 to 23.19 MPa (for geopolymer cements heated at 1000°C). The increase in the compressive strength from 17.14 to 23.19 MPa could be related to the sintering phenomenon which leads to the compact structure of the specimens, as discussed below.

3.2.6. Scanning electron microscopy

The micrographs of metakaolin-phosphate-based geopolymer cements cured at ambient temperature for 28 days and those heated at 200°C, 400°C, 600°C, 800°C and 1000°C are shown in Figure 9. It can be observed that the micrographs of all phosphate-based geopolymer cements are homogeneous and compact with coarse microstructure. It appears that berlinite contained in GPP1, phospho-tridymite and/or phospho-cristobalite contained in the heated geopolymer cements were embedded in the poly(phospho-siloxo) -Si-O-Si-O-P-O- matrix (Figure 9). The micrograph of GPP1 is a denser microstructure indicating the high connectivity of the poly(phospho-siloxo) network. The denser matrix is in agreement with the compressive strength results (Figure 8). The micrograph of GPP1 shows a white matrix of phosphate-based geopolymer cements which corresponds to the poly(phospho-siloxo) network -Si-O-Si-O-P-O- (Figure 9) rich in berlinite ($AlPO_4$). This corroborates with the result of the X-ray pattern of GPP1 (Figure 1) which shows some peaks of berlinite. The micrograph of GPP2 shows a white geopolymer matrix which corresponds to the poly(phospho-siloxo) network rich in Al (Figure 9). This confirms the formation of phospho-tridymite in the geopolymer cements GPP2, as can be shown clearly on the X-ray pattern of GPP2 (Figure 1). The morphology of the metakaolin-phosphate-based geopolymer cements GPP5 and GPP6 are more dense and compact microstructures due to high-temperature sintering. These compact microstructures correspond to the increase of the compressive strength (Figure 8). Rickard et al. [36,37] reported that the densification of geopolymer cements is due to the sintering of geopolymer matrix. This confirms the homogeneous and compact microstructures of GPP5 and GPP6 leading to an increase in compressive strength (Figure 8).

The micrographs of metakaolin-phosphate-based geopolymer cements soaked in water (GPP) and those cured at room temperature for 28 days are presented in Figure 10. These are compact,

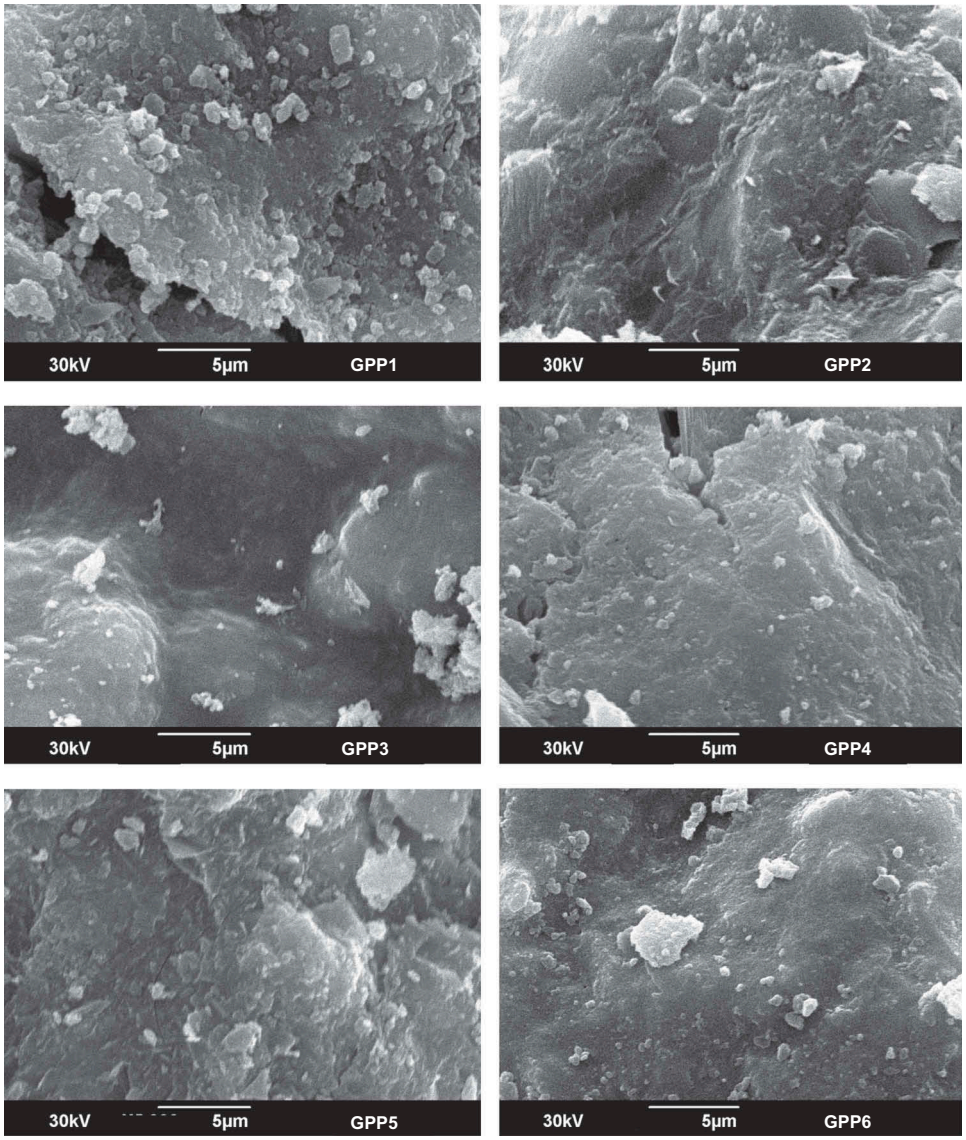


Figure 9. Micrographs of unheated and heated metakaolin-phosphate-based geopolymer cements.

homogeneous structure and exhibit some cracks like that of GPP1 (Figure 10). It was typically found that water does not affect the microstructure of the geopolymer cements. The presence of cracks observed on the micrographs of all metakaolin-phosphate-based geopolymer cements (Figures 9 and 10) could be related to the breakage of an integrated structure during the compressive strength measurement.

4. Conclusion

The kaolin used in this work was calcined at 700°C to obtain metakaolin. The prepared hardener (phosphoric acid solution) with molar concentration 10 M was used as a chemical reagent for producing metakaolin-phosphate-based geopolymer cements. The obtained geopolymer cements were cured at room temperature for 28 days. One part was heated at 200°C, 400°C, 600°C, 800°C and 1000°C and the others were soaked in water for 28 days. The results of the study showed that the compressive strength of the unheated metakaolin-phosphate-based geopolymer cements was higher than the ones heated at the temperatures 200°C, 400°C, 600°C, 800°C and 1000°C. Taking into consideration the standard deviation values, the compressive strengths are different therefore values are significant. The strength decreases from room temperature to 200°C due to the abrupt losses of the physically and the one part of chemically bonded water in their structure, it increases from 200°C to 400°C due the further polycondensation process, it decreases from 400°C to 600°C implying the disappearance of the hydroxyl groups. The sintering phenomenon that appears at the temperature between 600°C and 1000°C leads to the densification suggesting thus the increase of the strength. Despite the compressive strength of metakaolin-phosphate-based geopolymer cement soaked in water loss about 54% on its strength, the value of its strength remains higher (40.71 MPa) like Portland cement 42.5 suggesting thus this specimen could be used for the building materials. The X-ray pattern of unheated

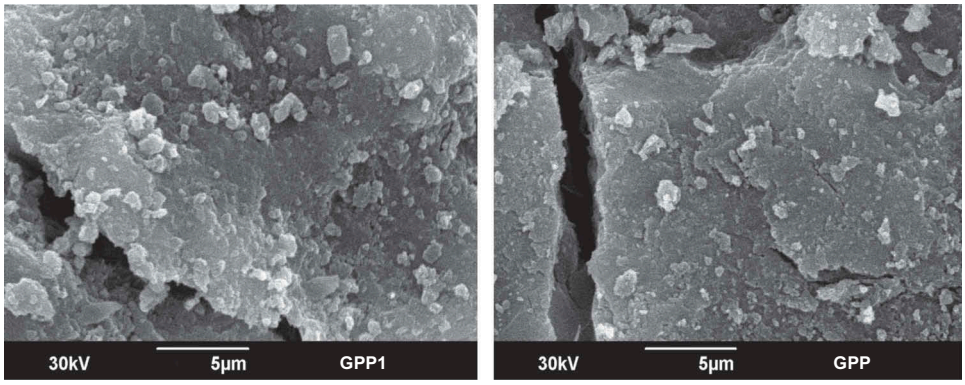


Figure 10. Micrographs of metakaolin-phosphate-based geopolymer cements cured at ambient temperature (GPP1) and the one soaked in water (GPP).

geopolymer cements shows the formation of a new crystalline phase such as berlinite which is transformed to phospho-tridymite and/or phospho-cristobalite during the calcination process. It could be shown that phospho-tridymite and/or phospho-cristobalite appear at low temperature (200°C). The micrographs of unheated and heated metakaolin-phosphate-based geopolymer cements are homogeneous and compact microstructure. It was found that the water affects the mechanical properties of metakaolin-phosphate-based geopolymer cements due to the hydrolysis of Si-O-P bonds.

Highlights

- The poly(phospho-siloxo) were prepared using metakaolin and phosphoric acid solution as raw materials.
- The compressive strengths of unheated poly (phospho-siloxo) were higher (87.96 MPa).
- The poly(phospho-siloxo) are water resistant and could be a high-temperature performance cements.
- The heated poly(phospho-siloxo) indicate the formation of phospho-tridymite and cristobalite at low temperature.
- The poly(phospho-siloxo) heated at 1000°C contains always structural water in its network.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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